

Preparation of some transition metal sulphides*

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Abstract. Ternary sulphides, LnMS_3 (Ln =rare earth metal; M =first row transition metal) and MV_2S_4 (M =Mg, Fe, Co, Ni and Zn) have been prepared by the reaction of appropriate ternary metal oxides with H_2S or CS_2/N_2 vapours at elevated temperatures. Chemical analysis and x-ray powder diffraction of the products indicate formation of single-phases with unique crystal structures in many cases.

Keywords. Transition metal sulphides, preparation; rare earth sulphides.

1. Introduction

Metal sulphides constitute an important class of solids crystallizing in a variety of structures and exhibiting a wide range of physical properties (Rao and Pisharody 1976). Many of them occur naturally as minerals: pyrite (FeS_2), chalcopyrite (CuFeS_2), molybdenite (MoS_2) for example. This class of solids offers immense scope for research towards understanding the interrelationship between structure and physical properties. For this purpose, convenient and reliable methods for the preparation of authentic samples are essential.

Transition metal sulphides are generally prepared by high temperature reaction of the constituent elements in sealed evacuated tubes. When the metal sulphide is quite stable, metathetical reaction between suitable components yields the product: for example, MoS_2 can be prepared by fusing MoO_3 with a mixture of sulphur and K_2CO_3 . The method of reacting elements in sealed tubes suffers from several disadvantages such as formation of multiphases, incomplete reaction and inhomogeneities in composition even where a single phase is obtained. Moreover, the method is not convenient for the synthesis of sulphides of rare earth metals in view of the difficulty in getting high-purity rare earth metals and their sensitivity to air and moisture.

We have developed methods for the synthesis of several ternary sulphides containing rare earth and transition metals based on the reaction of appropriate metal oxides with H_2S or CS_2 vapours at elevated temperatures. Preparation of some metal sulphides using H_2S and CS_2 vapour has been reported in the literature (Shafer 1972; Takahashi *et al* 1971; Lelieveld and Ijdo 1980).

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2. Experimental and Results

2-1. *Preparation of LnMS₃* (Ln = La, Nd, Gd; M = V, Cr, Mn, Fe, Co and Ni). The following LnMO_x oxides were prepared from high-purity binary oxides: LnVO₄, LnVO₃, LnCrO₃, LaMnO₃, LaFeO₃, LaCoO₃, LaNiO₃ and La₂Cu₂O₅. About 5g of LnMO_x taken in a graphite boat were placed in a alumina combustion tube held horizontally in a tubular furnace. For reaction with H₂S, dry H₂S from a Kipp's apparatus was passed over the sample (3-5 ml/min) while the furnace temperature was raised to the desired value (1000-1200°C). For reaction with CS₂ vapour, a stream of dry, oxygen-free, nitrogen was bubbled through CS₂. Nitrogen thus saturated with CS₂ was passed over the sample. Each sample was repeatedly heated with intermittent grinding until the reaction was complete (as indicated by constant weight). It generally took over 100 hrs of total reaction time for the reaction to be complete in many cases.

Chemical analysis (table 1) showed that in all the cases excepting copper, the composition of the sulphides was LnMS₃. In the case of copper, reaction of La₂Cu₂O₅ with H₂S yielded LaCuS₂ as the product. X-ray powder diffraction showed that the sulphides were monophasic with unique crystal structures. Among LaMS₃, M = V and Cr sulphides are isostructural crystallizing in a monoclinic structure while M = Mn, Fe, Co and Ni sulphides form another isostructural series having a hexagonal structure (Murugesan *et al* 1981).

2-2 *Preparation of M_xVS₂* (M = Mg, Fe, Co, Ni and Zn; x = 0.5 and 0.25). We have also prepared a series of metal-intercalated vanadium disulphides, M_xVS₂ (M = Mg, Fe, Co, Ni and Zn), by reaction of MV₂O₆ and MV₄O₁₁ with H₂S at 600-1000°C. Reaction of MV₂O₆ with H₂S gives M_{0.5}VS₂ while reaction of MV₄O₁₁ gives M_{0.25}VS₂. The sulphidation reaction involves simultaneous reduction of vanadium. For instance, MV₂O₆ + 6H₂S → MV₂S₄ + 6H₂O + 2 S. It must be mentioned that the composition of the sulphide is sensitive to reaction temperature. The higher the temperature the lower is the sulphur content of the product in general. Thus M_{0.25}VS₂ phases are formed at lower temperatures than M_{0.5}VS₂ phases. For a given M_xVS₂, iron, cobalt and nickel compounds are formed at lower temperatures while magnesium and zinc compounds require higher temperatures for their formation.

Table 1. Characterization of LnMS₃.

Compound	Sulphur (%)		Unit cell parameters			
	found	calculated	a (Å)	b (Å)	c (Å)	β (Å)
LaVS ₃	34.17	33.58	5.985	16.854	11.158	89.7
LaCrS ₃	33.55	33.45	5.970	17.110	11.033	87.5
LaMnS ₃	33.98	33.12	10.370	-	5.772	-
LaFeS ₃	33.33	33.02	10.314	-	5.806	-
LaCoS ₃	32.92	32.67	10.318	-	5.776	-
LaNiS ₃	32.59	32.68	10.295	-	5.762	-

Table 2. Characterization of MV_2S_4 .

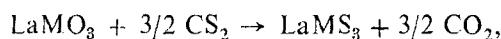
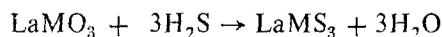
Compound	Sulphur (%)		Unit cell parameters			
	found	calculated	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (Å)
MgV ₂ S ₄	50.01	50.40	5.839	3.274	11.333	91.81
FeV ₂ S ₄	45.02	44.84	5.863	3.298	11.272	92.01
CoV ₂ S ₄	44.16	44.36	5.828	3.281	10.925	92.32
NiV ₂ S ₄	44.58	44.52	5.842	3.279	11.107	92.20

Chemical analyses show that the products are indeed MV_2S_4 and MV_4S_8 . X-ray diffraction data (table 2) reveal that MV_2S_4 sulphides are isostructural with V_3S_4 having vacancy-ordered NiAs-related structures (Oka *et al* 1978).

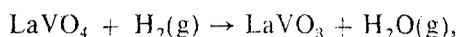
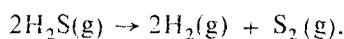
3. Discussion

The present study shows that the gas-solid reaction between H_2S or CS_2 vapours and metal oxides can be effectively used for the synthesis of ternary metal sulphides. The method thus obviates the necessity to use elements as starting materials and this is particularly an advantage in the preparation of rare earth containing sulphides.

Although sulphidation may be thought of as a direct reaction between the oxide and H_2S or CS_2 , e.g.,



dissociation of H_2S and CS_2 vapour to S_2 is likely to be an intermediate step, since it is known that S_2 molecules promote formation of sulphides (Swinnea and Steinfink 1980). Among the two sulphiding agents, H_2S seems to be appropriate for the synthesis of sulphides that involves simultaneous reduction of metal ions to lower oxidation states; for example, formation of $LaVS_3$ from $LaVO_4$ involves reduction of V^{5+} to V^{3+} :



Similarly during the formation of $BaVS_3$ from $Ba_2V_2O_7$, vanadium is reduced from 5+ to 4+ states.

With CS_2 reaction, deposition of carbon was found to occur in some cases especially when the flow rate is high.

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